On the Structure of the Line $\lambda = 6708$ A. of the Isotopes of Lithium.

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[Plate 4.]

I. *Introduction.*

From considerations based on known similarities between the series spectra of the alkali elements, it was to be expected that the members of the series $\nu = (1\cdot5, s) - (m, p)$ for lithium should consist of close doublets.

In 1913 Zeeman* investigated the absorption of the wave-length $\lambda = 6708$ A., the first member of the above series for this element, and found by the use of a concave grating of high resolving power that it consisted of a close doublet, with an estimated separation of $0\cdot144$ A. In the following year, Takamine and Yamada† also investigated the structure of this line, and found that it could be obtained in the form of a comparatively sharp doublet, with a separation of $0\cdot165$ A. In their experiments the source of radiation consisted of a brush discharge between iron terminals moistened with a 10 per cent. solution of LiCl. The spectral separation was measured with a 35-plate échelon grating.

In 1914 Kent‡ also investigated the wave-lengths $\lambda = 6708\cdot2$ A., $\lambda = 6103\cdot77$ A., $\lambda = 4972\cdot11$ A., and $\lambda = 4602\cdot37$ A., and found by the use of an échelon grating that all four wave-lengths consisted of doublets with the wave-length differences $0\cdot151$ A., $0\cdot114$ A., $0\cdot084$ A. and $0\cdot069$ A. respectively. He also found that in weak magnetic fields the members of the doublet $\lambda = 6708\cdot2$ were resolved into components of the types given by the sodium lines D_1 and D_2. With strong fields the magnetic resolution of the combined members of the doublet was that of a normal Zeeman triplet.

More recently, in 1916, King§ made a study of the structure of the lithium red line in the furnace spectrum of the vapour of this element with a ruled grating, and found again that it consisted of a doublet when a small

* Zeeman, 'K. Akad. Wetensch. Amsterdam, Proc.,' vol. 15, pp. 1130–1131 (1913).

† Takamine and Yamada, 'Proc. Tokyo Mathematico-Phys. Soc.,' 2nd Series, vol. 7, No. 18, p. 339 (1914).

‡ Kent, 'Phys. Zeit.,' vol. 15, p. 383 (1914).

§ A. S. King, 'Astrophys. Jour.,' vol. 28, p. 300 (1916).

quantity of lithium was used with a separation of 0·152 A. When high vapour densities were used, however, the line appeared as a triplet of variable separation from 0·25 to 0·36 A. In discussing his results King suggested that this variation in the interval of the triplet possibly originated in electrical resolution such as one obtains in the Stark effect.

Quite recently a study of the structure of the lithium red line was made by the writers by using a vacuum arc in lithium vapour as a source of radiation, and by using both Lummer plates and a 30-plate échelon grating crossed with a Lummer plate to effect the resolution.

In the course of this study it was found that when strong arcs were maintained in the vapour, the wave-length λ = 6708 A. consisted of a close quartet with separations of 0·128 A., 0·173 A. and 0·165 A.

II. *Apparatus.*

The apparatus used for producing the arc which is illustrated in fig. 1 consisted of a brass water-cooled chamber of the type shown in the diagram.
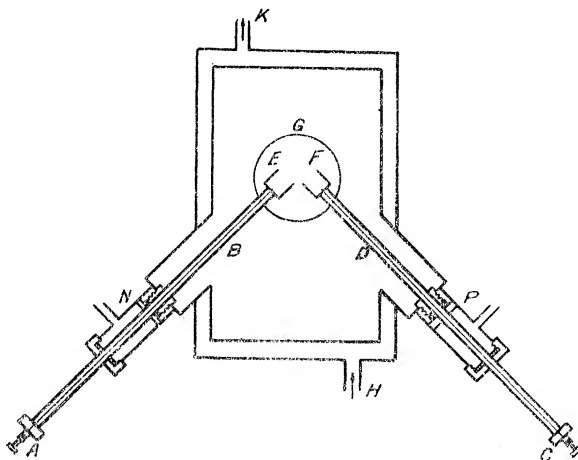

Fɪɢ. 1.

It was provided on opposite sides with windows of fused quartz, one of which is shown at G. The electrodes consisted of two steel cups, E and F, connected by wires to the binding poles A and C. These were supported by, but insulated from, two brass tubes B and D which in turn entered the lamp through two oil-sealed, close-fitting stuffing boxes. Preparatory to operating the arc, the cups E and F were filled with metallic lithium, and the chamber was highly exhausted with a set of Gaede rotary oil and mercury pumps. While the arc was in operation the pumps were kept running in order to clear away any gas given out by the electrodes. The arc was

started by bringing the two cups, E and F, into contact and then separating them. This vapourised the lithium and it was found that with currents of from 10 to 15 amps. from the 110 volt D.C. mains, strong steady arcs could easily be maintained in the vapour.

The échelon grating, the optical constants for which have been given in a previous paper,[*] consisted of 30 plates 1·004 cm. in thickness, with a width of step of 1 mm.

The data for the glass Lummer plate used are as follows :

Refractive indices.

$d = 0·448$ cm.

$\lambda = 6707·846 \times 10^{-8}$ cm.

$\mu = 1·50703$

$\partial\mu/\partial\lambda = -288·6$

$\Delta\lambda m = 0·4364 \times 10^{-8}$

6563·045 A.	1·50746
5896·155 A.⎫	1·50990
5890·186 A.⎭	
4861·49 A.	1·51560
4308·08 A.	1·52025

Dispersion formulæ used—

$$\mu = 1·491324 + \frac{82·2922}{\lambda - 1463·17}$$

and

$$\mu = 1·494199 + \frac{59·3239}{\lambda - 2089·47}.$$

III. *Observations.*

On several occasions during the investigation the spectrum of the radiation issuing from the arc was photographed with a quartz spectrograph. The spectrum obtained is shown in " b " (Plate 4, fig. 2). It consisted of the wave-lengths $\lambda = 6707·846$ A., $\lambda = 6103·377$ A., $\lambda = 4602·37$ A., $\lambda = 4132·44$ A. and $\lambda = 3232·77$ A.

In order to isolate the light of the red line, a Wratten filter, No. 70, was used. From the reproduction shown in (a), fig. 2, it will be seen that the filter sufficed to cut off all light issuing from the arc other than that of the red line.

The diffraction pattern of the red line as analysed by our Lummer plates is shown in Plate 4, fig. 3. It consists of the doublet ordinarily observed with members at a and b, and a third member at c, *i.e.*, in so far as resolution by the Lummer plate revealed its structure the red line consisted of a triplet.

When, however, the line was resolved by the échelon, crossed with a Lummer plate, observation showed it to consist of a quartet. The reason the Lummer plate did not reveal the quartet structure was due to the fact that

* McLennan, 'Roy. Soc. Proc.,' A, vol. 87, p. 269 (1912).
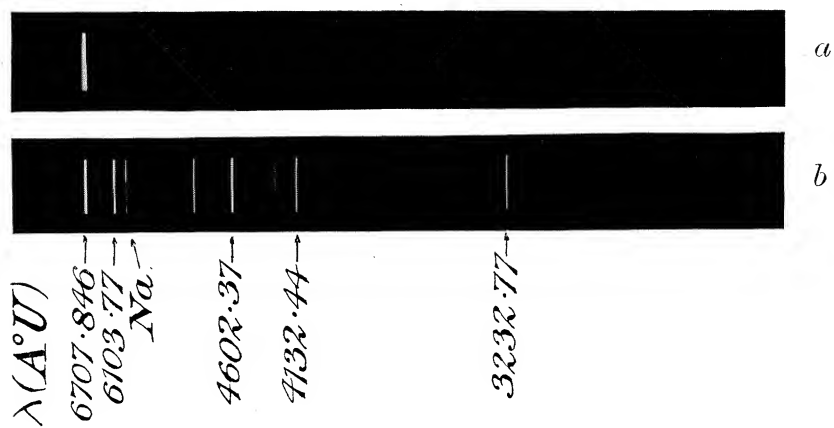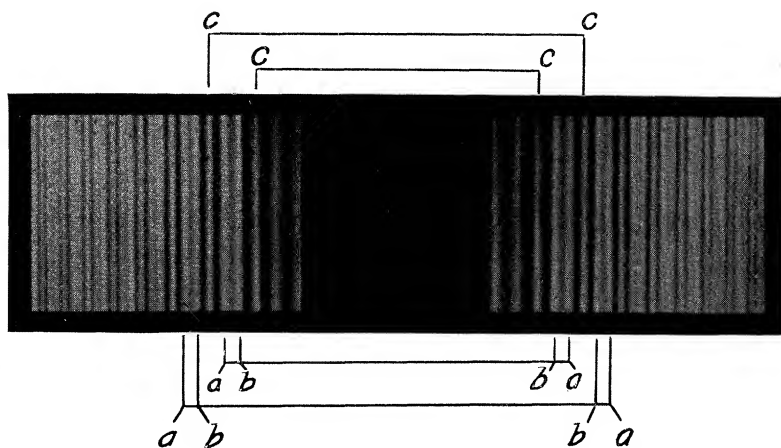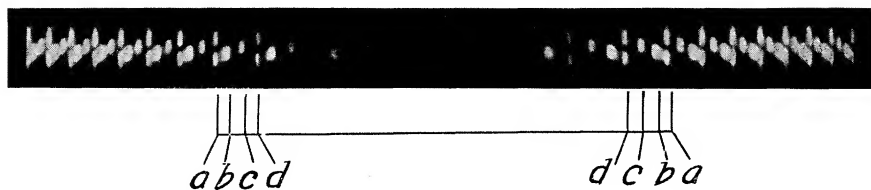
FIG. 2.

FIG. 3.

FIG. 4.

the member of shortest wave-length of the quartet of one order overlapped or lay close to the member of longest wave-length of the quartet in the next lower order of the diffraction pattern.

An enlarged reproduction of the pattern obtained with the échelon crossed with the Lummer plate is shown in Plate 4, fig. 4. In it the members *a* and *b* constitute the doublet of the red line as ordinarily observed, and *c* and *d* constitute the new doublet revealed by this investigation.

From measurements made on several plates, the separation between the members *a* and *b* was found by the formula $\Delta\lambda = [\delta(\alpha^2)/\Omega_1]\Delta\lambda_m$* to be 0·128 A.; that between the members *a* and *c* 0·301 A. and that between the members *c* and *d* 0·165 A.

IV. *Discussion of Results.*

(a) *Isotope Doublets.*—In the recent discussion† on isotopes at the Royal Society, Merton, commenting on the fact that the line 6708 A. emitted by lithium, consisted of two components, approximately 0·151 A. apart, stated that if lithium is accepted as a mixture of two isotopes of atomic weights 6 and 7, calculations based on Bohr's theory showed that each of the components of the doublet should be accompanied by a satellite some sixteen times as faint and displaced by 0·087 A. He also stated that he had sought for these satelites but had not been able to observe them. In view of the observation by us of a new doublet accompanying the ordinary doublet of λ = 6708 A., the question of its origin being associated with the isotope of lithium naturally arises.

It is known that with magnetic fields of moderate intensity the sodium line D_1 is resolved into a quartet and the D_2 line into a sextette. As stated above Kent found that the members of the doublet λ = 6708 A. (as ordinarily observed) showed magnetic resolutions in weak fields of the same types as the D_1 and D_2 lines. If, then, we ascribe the two doublets found in our investigations to the isotopes Li^6 and Li^7, our observations would go to show that the members *a* and *b* noted on our plates originated in the same isotope of lithium. If we ascribe the newly observed doublet with members *c* and *d* to the second isotope of lithium, it will be noted that since it appears on the short wave-length side of the doublet *a*, *b*, it would follow from Bohr's theory that the doublet *a*, *b*, should be ascribed to Li^6 and the doublet *c*, *d*, to Li^7, *i.e.*, the radiations from Li^7 should be of shorter wave-length than corresponding ones from Li^6.

(b) *Separations of Doublets.*—On this view it will be seen that from our

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* McLennan and McLeod, 'Roy. Soc. Proc.,' A, vol. 90, p. 246 (1914).

† 'Roy. Soc. Proc.,' A, vol. 99, p. 87 (1921).

measurements the separation of the Li^6 doublet is 0·128 A. and that of the Li^7 doublet 0·165 A.

Observations on corresponding series lines in the spectra of Na, K, Rb and Cs have made it clear that the doublet frequency differences with these elements are directly proportional to the squares of the atomic weights. If this law be applicable to lithium it would follow that wave-length differences for the two doublets of Li^6 and Li^7 at $\lambda = 6708$ A. should be approximately 0·55 A., which it will be seen is between three and four times the doublet separations observed in our experiments. The values obtained by us, however, for the separations of the two doublets are of interest in connection with this law, for according to it the separations for the Li^7 and Li^6 doublets should be in the ratio 49/36, *i.e.*, 1·36 : 1·00. As the ratio of the separations found by us was 1·30 it will be seen there is fair agreement.

(c) *Displacement of Isotope Doublets.*—It will be noted that from our measurements the average displacement of the Li^7 doublet *c* and *d* was about 0·32 A. on the shorter wave-length side of the Li^6 doublet *a* and *b*. This displacement is, therefore, between three and four times as great as the calculated separation given by Merton, namely, 0·087 A.

(d) *Isotope Displacement and Atomic Number.*—In 1917, Aronberg[*] in studying the line $\lambda = 4058$ A., emitted by a specimen of radio-lead of atomic weight 206·3318, observed a difference of 0·0044 A. between the wave-length emitted by this specimen and that emitted by ordinary lead of atomic weight 207·29. This result was also confirmed by Merton,[†] who found a difference of wave-length for radio-lead from pitchblende and ordinary lead of 0·0050 ± 0·0007 for the same wave-length. As the difference in wave-length one would expect to obtain in this case on the Bohr theory for the line $\lambda = 4058$ is 0·00005 A., it will be seen that the observed wave-length difference was between eighty and ninety times as great as the calculated amount.

Taking this result in conjunction with our own observations on lithium, it would appear that with lead and lithium the observed isotope displacements can be very closely obtained by multiplying the displacements calculable on the Bohr theory by the atomic numbers of the respective elements.

If it should turn out that such a law were applicable generally to isotopic displacements, it would bring the spectral isotopic displacements of a number of the elements easily within the scope of observation open to us, with high

* 'Aronberg, 'Proc. Nat. Acad. Sc.,' vol. 3, p. 710 (1917); 'Astrophys. Jour.,' vol. 47, p. 96 (1918).

† Merton, 'Roy. Soc. Proc.,' A, vol. 96, p. 388 (1 20).

resolution ruled gratings and with échelon gratings and Lummer plates of the resolving powers already developed.

(e) *Intensity of Doublet Components.*—During the course of the experiments visual comparisons were frequently made of the relative intensities of the members of the quartet. It was noted that irregular fluctuations in these relative intensities always accompanied variations in the strength of the current in the arc. When the arc was steady and at its brightest, the members *b* and *d* appeared with the greatest relative intensity, *i.e.*, the shorter wave-length member of both the Li^6 doublet and of the Li^7 doublet, appeared to be of stronger intensity than the longer wave-length members of these doublets. Of all four members of the quartet the component " *b* " (the shorter wave-length member of the Li^6 doublet) always possessed the greatest intensity. This result for each of the doublets is in keeping with observations made on the relative intensities of the D_1 and D_2 lines, in the spectrum of sodium. Voss,[*] who has made a careful investigation of this point, found D_2 to be always the more intense of the D lines, with a maximum value for the ratio of the intensities $D_2/D_1 = 2$ correct to within 10 per cent.

(f) *Identity of Components.*—As the chemically determined atomic weight of lithium is 6·94, it would appear that in ordinary samples of lithium there should be present about sixteen times as much of the Li^7 type as of the Li^6 form. With this in mind one might expect the lines of Li^7 to be of greater intensity than those of Li^6. This would mean, on the view of the identity of the components taken above, that the members *c* and *d* should be of stronger intensity and be more persistent with low arc currents than the members *a* and *b*. The results of our observations, however, were directly opposed to this conclusion.

Another view to take of the identity of the components of the quartet would be to ascribe the components *a* and *c* to Li^6 and the components *b* and *d* to Li^7. This would make our observations on the relative intensities of the components fit in with the relative amounts of Li^6 and Li^7 present in lithium, as determined by the chemically measured atomic weight of the element. On this basis the doublet separation for Li^6 would be 0·301 A., and that for Li^7 0·338 A., values that are nearer to the value 0·55 A. calculated on the basis of the law known to hold for the other alkali elements. The isotopic separation on this view would be between 0·128 A and 0·165 A.

* Voss, ' Phys. Rev.,' vol. 11, No. 1, p. 21 (January, 1918).

V. *Observations on other Wave-lengths.*

A cursory examination was made of the structure of other lines in the spectrum of lithium, and it was found that the wave-length $\lambda = 6103\cdot77$ A. consisted of at least three well defined components. It was found difficult to make accurate visual observations as regards the wave-length $\lambda = 4602\cdot37$ A., but it was definitely seen to be resolved and consequently it had as a minimum two components. Detailed results of the measurements being made on these wave-lengths will appear in a later communication.

We desire to express our indebtedness to Mr. J. F. T. Young for calculations on the dispersion of the Lummer plate used in the experiments, and to Miss Cale and Mr. P. Blackman for assistance in preparing the illustrations in this paper.

Interfacial Tension and Hydrogen-Ion Concentration.

By H. HARTRIDGE and R. A. PETERS.

CONTENTS.

Section 1.—INTRODUCTION.

The predominance of hydrogen-ion concentration (1) in the colloidal chemistry of the proteins and other substances (Loeb (2)) makes imperative an investigation of those changes at the interface between two phases which are brought about by changes in hydrogen-ion concentration. Previous investigators have directed their attentions to the purely chemical aspects of the interfacial tension between soap solutions and oils, or to non-reactive chemical substances, such as benzene. Using a drop-weight method of measuring interfacial tension, Donnan (3) showed that crude rape oil and crude olive
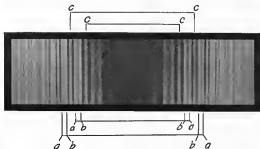
λ(A·U')

6707·846
6103·77
Na

4602·37

7132·44

3233·77

Fig. 2.

Fig. 3.

Fig. 4.